

NICKEL ACTIVITY IN SILICATE LIQUIDS: SOME PRELIMINARY RESULTS

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ABSTRACT

The activity coefficient of nickel oxide (γ_{NiO}) in a number of silicate liquids has been determined by equilibrating the liquid with a Ni-Fe alloy at a known $f(\text{O}_2)$. Two series of experiments were carried out. *Series 1*: Eighteen silicate liquids, ranging in composition from high-Mg basalt to dacite, were run at constant temperature (1300°C) and $f(\text{O}_2)$ ($\log f(\text{O}_2) = -8.20$) to assess the influence of composition on γ_{NiO} . The activity coefficient varies from 7.8 in the high-Mg basalt to 30 in the dacite. The increase in γ_{NiO} with the acidity of the liquid is ascribed to the decreasing number of octahedral sites in the liquid. *Series 2*: Four of the liquids used in Series 1 were run at a constant CO_2/H_2 ratio at temperature intervals of 50° between 1200 and 1400°C. Within the accuracy and temperature range of the experiments, γ_{NiO} is proportional to the absolute temperature, provided the melt composition remains constant. As the activity of NiO is a measure of the solubility of Ni in a silicate liquid, it can be used as an aid to predicting the Ni content of phases that crystallize from that liquid. Both the partitioning (D) of Ni between olivine and silicate liquids and the distribution coefficient (K_D) for Ni between immiscible sulfide and silicate liquids are considered as examples. Both parameters are strongly dependent on temperature and, to a lesser extent, on the composition of the silicate liquid.

SOMMAIRE

Le coefficient d'activité γ_{NiO} de l'oxyde de nickel a été déterminé pour plusieurs liquides silicatés, par équilibration avec un alliage Ni-Fe à fugacité d'oxygène $f(\text{O}_2)$ connue. Dans une première série d'expériences, dix-huit compositions, allant de basalte magnésien à dacite, ont été maintenues à température et fugacité constantes [1300°C; $\log f(\text{O}_2) = -8.20$], en vue d'établir l'effet de la composition sur γ_{NiO} . Ce coefficient varie de 7.8 (basalte magnésien) à 30 (dacite). L'accroissement de γ_{NiO} avec l'acidité du liquide doit être fonction de la diminution du nombre des sites octaédriques

dans le liquide. Quatre de ces liquides ont ensuite été étudiés à rapport CO_2/H_2 constant, entre 1200 et 1400°C, à intervalles de 50°. Dans ce domaine de température et dans les limites de précision des mesures, γ_{NiO} est proportionnel à la température absolue, lorsque la composition reste constante. Vu que l'activité du NiO mesure la solubilité du nickel dans un bain fondu silicaté on peut s'en servir pour prédire la teneur en Ni des phases qui s'en séparent par cristallisation. La répartition (D) du Ni entre olivine et liquide silicaté, et le coefficient de partage K_D du Ni entre liquides immiscibles (silicaté et sulfuré), considérés à titre d'exemples, dépendent tous deux fortement de la température et, à un degré moindre, de la composition du liquide silicaté.

(Traduit par la Rédaction)

INTRODUCTION

Activity coefficients (γ) for certain metal oxides in silicate liquids can be measured by equilibrating the liquid with the pure metal or metal alloy at a known $f(\text{O}_2)$. Metallurgists have been carrying out experiments of this type for a number of years and have determined metal oxide activity coefficients in several simple silicate systems of metallurgical interest *e.g.*, Grimsey & Biswas 1976, 1977a, Schuhmann & Ensio 1951, Turkdogan 1962, Bodsworth 1959, Wang & Toguri 1974, Nagamori 1974). Despite the obvious importance of these types of data, few measurements have been made on natural silicate liquids. Roeder (1974) and Nolan (1977) have determined γ_{FeO} in a number of basaltic liquids and Duke & Naldrett (1977) reported γ_{NiO} for four liquids ranging in composition from basalt to rhyolite.

This paper reports γ_{NiO} determinations at constant temperature and $f(\text{O}_2)$ for eighteen silicate liquids ranging in composition from high-Mg basalt to dacite. Four of these liquids were also run at a constant CO_2/H_2 ratio at temperature intervals of 50° between 1200 and 1400°C.

The results are used to calculate the influence of temperature and melt composition on the partitioning of Ni between olivine and basaltic liquids and between immiscible sulfide and silicate liquids.

EXPERIMENTAL TECHNIQUES

NiO activities (a_{NiO}) were determined by equilibrating silicate liquids with a Ni-Fe alloy at a known $f(\text{O}_2)$. The governing equation is:



for which the equilibrium constant

$$K_1 = \frac{a_{\text{NiO}}}{a_{\text{Ni}} \cdot f(\text{O}_2)^{\frac{1}{2}}} \quad (2)$$

so that $a_{\text{NiO}} = K_1 \cdot a_{\text{Ni}} \cdot f(\text{O}_2)^{\frac{1}{2}}$ (3)

K_1 was calculated from the free-energy equation given by Nagamori & Mackey (1978) using solid Ni and NiO as the standard states (Table 1).

TABLE 1. FREE ENERGY VALUES

Reaction	ΔG	Source
Ni(s) + $\frac{1}{2}\text{O}_2(\text{g}) = \text{NiO}(\text{s})$	-56075 + 20.46T	1
Fe(s) + $\frac{1}{2}\text{O}_2(\text{g}) = \text{FeO}(\text{l})$	-55119 + 10.69T	2 & 3
Ni(s) + $\frac{1}{2}\text{S}_2(\text{g}) = \text{NiS}(\text{l})$	-25560 + 9.70T	4
Fe(s) + $\frac{1}{2}\text{S}_2(\text{g}) = \text{FeS}(\text{l})$	-28772 + 8.27T	5
Mg(s) + $\frac{1}{2}\text{O}_2(\text{g}) = \text{MgO}(\text{s})$	-175302 + 49.57T	5
2Ni(s) + Si(s) + 2O ₂ (g) = Ni ₂ SiO ₄	-328250 + 82.00T	4
2Mg(s) + Si(s) + 2O ₂ (g) = Mg ₂ SiO ₄	-529617 + 140.66T	5
2Fe(s) + Si(s) + 2O ₂ (g) = Fe ₂ SiO ₄	-327136 + 60.26T	5
2Ni(s) + SiO ₂ (cryst) + O ₂ = Ni ₂ SiO ₄	-124072 + 47.62T	6
NiO(s) + $\frac{1}{2}\text{SiO}_2(\text{glass}) = \text{NiSi}_2\text{O}_7$	-1275 + 0.79T	6
Fe ₂ SiO ₄ (s) + $\frac{1}{2}\text{SiO}_2(\text{glass}) = 2\text{FeSi}_2\text{O}_7$	-3034 + 2.10T	7
Mg ₂ SiO ₄ (s) + $\frac{1}{2}\text{SiO}_2(\text{glass}) = 2\text{MgSi}_2\text{O}_7$	4732 - 2.73T	7
Si(s) + O ₂ (g) = SiO ₂ (glass)	-215218 + 40.43T	5
Si(s) + O ₂ (g) = SiO ₂ (cryst)	-215014 + 40.47T	5

1 = Nagamori & Mackey 1978; 2 = Schuhmann & Ennio 1951; 3 = Coughlin 1954; 4 = Mah & Prankratz 1976; 5 = Robie et al. 1978; 6 = Campbell & Roeder 1967; 7 = Nicholls et al. 1971. T in °K.

For the calculation of activity coefficients it is desirable to have a knowledge of speciation in natural silicate liquids. The present state of knowledge of the structure of silicate liquids is poor and, in the absence of a specific model, mole fractions of conventional oxides (NiO, MgO, Al₂O₃, SiO₂, etc.) have been used throughout this paper; γ_{NiO} has therefore been calculated from the equation

$$a_{\text{NiO}} = X_{\text{NiO}} \gamma_{\text{NiO}} \quad (4)$$

It is convenient to express the Ni in the melt as NiO for two reasons: (i) Distribution and partition coefficients for Ni are most readily expressed in terms of equations involving NiO. (ii) Reliable free-energy data are available for

NiO; they are not for many of the other possible Ni species in the melt. We do not mean to imply that NiO exists as the dominant Ni species in the melt; in fact, the high activity coefficients obtained in this study would suggest that it does not. Ni²⁺ or Ni-silicate complexes are more likely species. Similarly, the calculations of γ_{FeO} , γ_{MgO} and γ_{SiO_2} , presented later in the paper, do not necessarily imply the existence of 'FeO', MgO and SiO₂ as species in the melt.

The charges were run as beads of liquid on a Ni metal loop (99.999% Ni) using a surface-tension technique similar to that described by Presnall & Brenner (1974). Samples were quenched in the gas mixture at the top of the furnace. No quench crystals were observed.

A series of experiments using differing run times showed that equilibrium is achieved in 8 hours at 1280°C. Experiments above this temperature were run for a minimum of 16 hours and those below for at least 40 hours. The effectiveness of the 16-hour run duration was confirmed by approaching equilibrium from both high and low $f(\text{O}_2)$ in one of the experiments.

The oxygen fugacity was controlled by mixing CO₂ and H₂ using the method described by Darken & Gurry (1945). The gases used were "Bone Dry" CO₂ and "Prepurified" H₂, both supplied by Matheson of Canada Ltd. Calibration of the gas mixture was checked against the iron-wüstite equilibrium at monthly intervals over the duration of the experiments. Values for the CO₂/(CO₂+H₂) mixture required to achieve this equilibrium ranged from 37.10% to 37.80% at 1200°C, giving a log $f(\text{O}_2)$ of -11.95 ± 0.02 . The gas mixture used for most of the runs was checked with a zirconia cell and found to agree within 0.01 log units. Oxygen fugacities are believed accurate to within 0.02 log units, introducing an error of less than 2% in the calculated a_{NiO} . The thermocouple was standardized against the melting point of gold (1064°C) and against a National Bureau of Standards thermocouple. Temperatures are believed accurate to within $\pm 2^\circ\text{C}$.

Run products were analyzed by an ARL-AMX and EMX electron microprobe. Glasses were analyzed with an energy-dispersive spectrometer at 15 kV using the matrix correction procedure described by Bence & Albee (1968). The Ni content of the glass and the Fe content of the Ni wire were determined with wavelength-dispersive spectrometers using pure Fe and Ni as standards at 20 kV. The EMPADR VII program of Rucklidge & Gasparrini (1969) was used to correct the raw data.

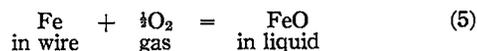
During the experiments some of the Fe in the silicate liquid entered the Ni wire to form a

Ni-Fe alloy. Consequently, at the end of a run, the Ni wire contains about 2% Fe. The Fe content of the Ni wire usually shows some evidence of zoning, with the centre of the wire containing appreciably less Fe than the edge. This is because the rate of diffusion in the solid wire is low compared with that in the liquid, resulting in a dynamic equilibrium between liquid and the Ni-Fe alloy at the edge of the wire. Following Grimsey & Biswas (1977a) we have assumed that the a_{Ni} in the silicate liquid is the same as that at the edge of the Ni-Fe wire. Activity coefficients of Grimsey & Biswas (1977b), between 1.00 and 0.99 over the range of interest, were used to calculate the a_{Ni} at the edge of the wire. As the Ni distribution between the liquid and the edge of the wire is reversible, we are confident that the a_{NiO} is accurate to within $\pm 5\%$.

Loss of Fe to the Ni wire and some volatilization of the alkalis have resulted in FeO, Na₂O and K₂O being lower in the silicate run products than in the original samples. As a consequence,

the other elements are correspondingly enriched. Thus an andesite, after equilibrating with Ni wire, has a SiO₂ content close to that of a dacite and a dacite, a SiO₂ content approaching that of a rhyolite.

The Fe content of the Ni-Fe wire can potentially be used to calculate the activity coefficient of FeO (γ_{FeO}) in the silicate liquid. From the reaction



it can be shown that

$$a_{FeO} = K_5 \cdot f(\text{O}_2)^{\frac{1}{2}} \cdot a_{Fe} \quad (6)$$

where K_5 is the equilibrium constant for equation (5). The a_{Fe} can be calculated from the composition of the wire and the activity coefficients given by Grimsey & Biswas (1977b) for Ni-Fe alloys at 1300°C. Values for γ_{FeO} , calculated from equation (6) and the mole fraction of FeO (X_{FeO}) of the silicate liquids, are given in Table 2. No allowance has been made

TABLE 2. ANALYSES OF GLASS AND NI-Fe ALLOYS FOR THE 1300°C RUNS

Run No.	A1.1	A1.2	A1.3	A1.4	A2.1	A2.2	A2.3	A2.4	A3.5	A3.6	A3.7	T4.6	T4.5	T4.7	T4.8	T12.1	T12.2	T12.3	T12.4	Run No.
Sample	GRB4(a)	401	1868	65b	S43	B711	NLB	B65	CRB	MHA	GOB	S43	306	And	Dac	P227	SY-MN	N144	SY-CRB	Sample
Temp. °C	1300	1300	1300	1300	1301	1301	1301	1301	1302	1302	1302	1300	1300	1300	1300	1300	1300	1300	1300	Temp. °C
log f_{O_2}	-8.20	-8.20	-8.20	-8.20	-8.19	-8.19	-8.19	-8.19	-8.18	-8.18	-8.18	-8.20	-8.20	-8.20	-8.20	-8.20	-8.20	-8.20	-8.20	log f_{O_2}
Time (hr)	20	20	20	20	48	48	48	48	40	40	40	20	20	20	20	21	21	21	21	Time (hr)
GLASS																				
SiO ₂	52.9	53.9	50.6	50.4	56.8	52.7	52.3	51.6	55.1	62.4	50.7	57.2	52.8	67.9	78.5	52.2	50.8	54.9	58.7	SiO ₂
Al ₂ O ₃	15.9	16.5	14.6	12.6	18.4	17.1	13.4	16.7	15.7	17.8	17.1	18.5	15.5	16.0	12.1	14.1	12.6	13.5	18.8	Al ₂ O ₃
TiO ₂	3.3	2.1	2.2	2.8	1.6	0.7	2.8	2.9	1.9	0.9	2.5	1.5	0.5	1.4	0.3	1.0	11.1	0.6	-	TiO ₂
FeO	6.3	7.2	6.1	7.0	3.1	4.8	6.6	4.7	6.7	2.2	5.7	4.4	6.5	2.5	1.0	6.5	0.0	5.9	-	FeO
MnO	0.3	0.2	0.2	0.3	0.1	0.3	0.2	0.3	0.2	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.4	0.5	-	MnO
MgO	6.3	6.6	10.0	10.0	4.8	8.1	8.2	8.3	4.9	3.1	9.0	5.0	10.4	1.6	0.4	9.8	7.6	10.4	6.4	MgO
CaO	9.9	9.3	10.8	10.4	9.3	11.6	11.5	10.1	9.9	6.6	10.6	9.3	10.3	3.5	1.4	10.8	11.7	10.0	11.4	CaO
Na ₂ O	1.7	1.8	0.7	1.4	1.7	1.1	1.0	1.3	1.7	2.9	1.5	2.0	0.9	3.3	4.2	1.5	0.8	1.0	-	Na ₂ O
K ₂ O	0.7	0.9	0.3	0.4	0.7	0.4	0.3	0.7	0.5	1.1	0.2	0.6	0.2	1.5	1.3	0.0	0.2	0.3	-	K ₂ O
NiO	2.02	1.92	2.35	2.28	1.80	2.09	2.26	2.13	1.80	1.12	2.08	1.88	2.51	1.09	0.65	2.18	2.51	2.16	1.91	NiO
Total	99.3	100.4	97.9	97.6	98.3	98.9	98.6	98.7	98.4	98.1	99.5	100.5	99.7	98.8	100.0	98.2	97.7	99.3	97.2	Total
Si/O	.315	.315	.307	.310	.330	.313	.316	.308	.328	.355	.302	.329	.313	.378	.419	.315	.303	.325	.338	Si/O
X _{NiO}	.0173	.0162	.0198	.0193	.0157	.0177	.0190	.0181	.0156	.0098	.0173	.0161	.0207	.0096	.0056	.0183	.0215	.0178	.0165	X _{NiO}
Y _{NiO}	9.2	9.9	8.1	8.3	10.4	9.2	8.5	9.0	10.4	16.8	9.3	10.0	7.8	17.0	30.0	8.7	7.7	9.0	10.1	Y _{NiO}
X _{FeO}	.056	.063	.053	.061	.028	.042	.058	.042	.060	.0204	.050	.039	.056	.0232	.0088	.957	-	.050	-	X _{FeO}
Y _{FeO}	1.30	1.49	1.29	1.31	1.25	.77	.79	.88	1.03	1.00	.85	1.19	.94	1.42	1.45	1.31	-	1.40	-	Y _{FeO}
NI WIRE																				
Wt. % Fe	2.17	2.60	2.10	2.32	1.02	1.24	1.59	1.36	1.95	.87	1.57	1.60	1.75	1.25	.60	2.23	-	2.15	-	Wt. % Fe
X _{Fe}	.0228	.0273	.0221	.0244	.0107	.0130	.0167	.0143	.0205	.0091	.0165	.0168	.0184	.0131	.0061	.0234	-	.0226	-	X _{Fe}
a _{FeO}	.0727	.0927	.0685	.0797	.0349	.0325	.0459	.0369	.0615	.0205	.0426	.0464	.0524	.0329	.0128	.0745	-	.0700	-	a _{FeO}
a _{NiO}	.160	.160	.161	.160	.163	.162	.162	.163	.162	.164	.162	.161	.161	.163	.165	.160	.166	.166	.166	a _{NiO}

for the Fe_2O_3 content of the liquid, so that the γ_{FeO} values in Table 2 should be slightly below the true values. Stoichiometric liquid 'FeO' was used as the standard state for FeO to facilitate a comparison between these results and those of Roeder (1974). Although the comparison is reasonable the results should be regarded as preliminary as (1) γ_{Fe} is not well known in Ni-Fe alloys at low Fe contents and (2) there

is some doubt as to the degree to which Fe has equilibrated between the wire and the liquids in some of the runs. Free-energy values and standard states used to calculate the equilibrium constants in this paper are given in Table 1.

RESULTS

Two series of experiments are reported in this

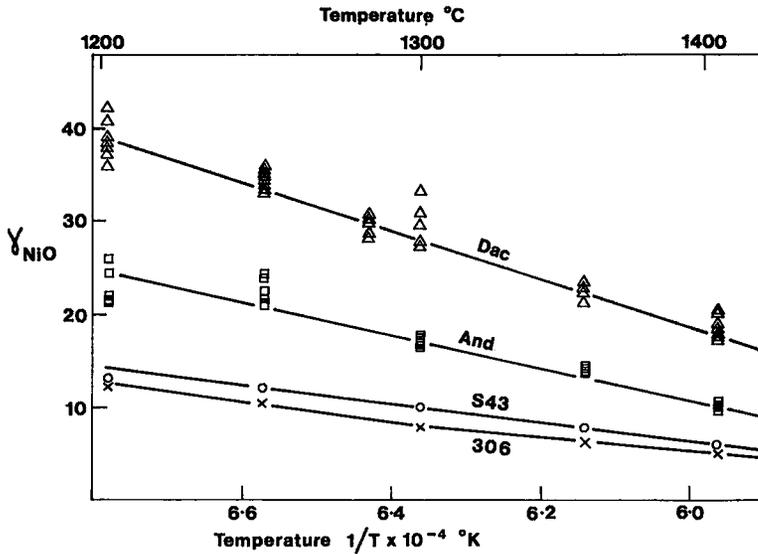


FIG. 1. A plot of γ_{NiO} against $1/T$ (K) for the four samples studied in Series 2.

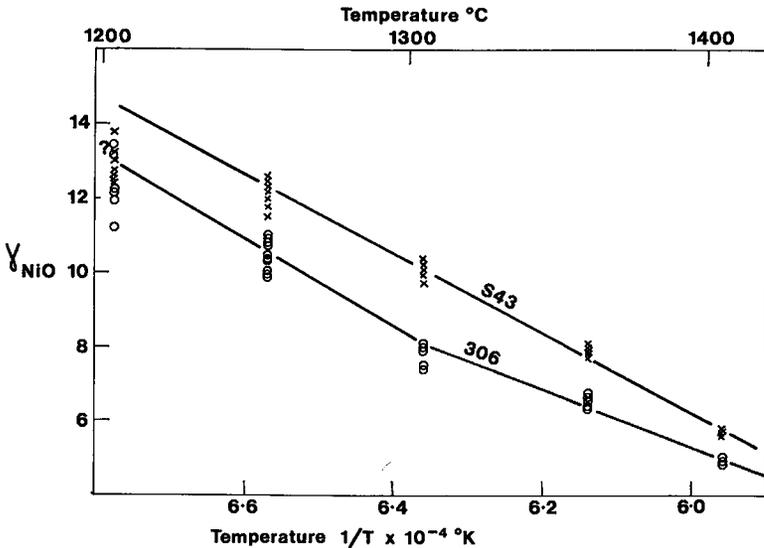


FIG. 2. An enlargement of part of Fig. 1 showing samples S43 and 306 in greater detail.

TABLE 3. GLASS COMPOSITION OF 1203°C RUNS

Sample	306	S43	And	Dac
SiO ₂	56.6	55.8	67.9	77.8
Al ₂ O ₃	14.8	16.7	16.6	12.1
TiO ₂	0.5	1.6	1.5	0.2
FeO	4.6	6.3	2.2	1.6
MnO	0.2	0.3	0.1	0.0
MgO	6.1	5.6	1.7	0.1
CaO	11.8	8.9	3.8	1.9
Na ₂ O	1.3	2.1	2.8	4.5
K ₂ O	0.2	0.7	1.6	1.5
NiO	1.17	1.12	0.6	0.37
Total	97.3	99.1	98.8	100.1

paper. The first was carried out at constant temperature and $f(\text{O}_2)$, with the aim of assessing the influence of composition on γ_{NiO} in silicate liquids. The second series consisted of a detailed study of the influence of temperature on γ_{NiO} for four of the samples used in the first series.

Series 1

Natural samples ranging in composition from high-Mg basalt to dacite and two Fe-free synthetic liquids were run at 1300°C and a log $f(\text{O}_2)$ of -8.20. The results are presented in Table 2; γ_{NiO} ranges from 7.7 in a high-Ti synthetic liquid (SY-MN) to 30 in the 'dacite' (Dac). There is, however, little variation in γ_{NiO} for liquids of basaltic composition, the majority lying between 8.0 and 10.0 at 1300°C.

Series 2

A high-Mg basalt (306), an Archean tholeiite (S43), an andesite (And) and a dacite (Dac) were run at temperature intervals of 50° between 1200 and 1400°C and at an $f(\text{O}_2)$ controlled by the gas-mixing ratio used in series 1 [$\text{CO}_2/(\text{CO}_2+\text{H}_2) = 86.44\%$]. Three of the samples were free of crystals but the fourth, the high-Mg basalt, had olivine crystals in both the 1200 and 1250°C runs. The γ_{NiO} (relative to solid NiO as the standard state) was calculated at each temperature; the results are plotted in Figures 1 and 2. Within the accuracy of the experiments there is a straight-line relationship between γ_{NiO} and $1/T$ for the three samples that did not contain crystals. Variations in alkali and FeO loss in the different experiments have re-

sulted in liquids of slightly different composition and have contributed to the scatter in the data, but the losses do not vary systematically as a function of temperature. Considering these variations, the linear fit to the data is excellent. Crystallization of olivine from the high-Mg basalt lowered its Mg content and raised its SiO₂, Al₂O₃ and alkali contents, resulting in an increase in γ_{NiO} . By 1200°C olivine crystallization has modified the liquid to a composition similar to S43 (Table 3). As a consequence γ_{NiO} is similar in both samples at 1200°C.

DISCUSSION

The high γ_{NiO} values obtained in this study do not necessarily indicate a true departure from Raoult's law but rather suggest that NiO is not an important species in the melt. Nevertheless, if γ_{NiO} can be predicted as a function of temperature and composition, it is possible to construct an internally consistent model to calculate partition and distribution coefficients for Ni, assuming NiO is the melt species.

Roeder (1974) has shown that γ_{FeO} in basaltic liquids ranges from 0.9 to 2.0. These values are appreciably less than basaltic γ_{NiO} values, even after allowing for differences in the standard states used for FeO (liquid) and NiO (solid). The higher activity coefficients for NiO indicate that it has a greater tendency to leave the liquid than FeO. The significance of this difference is most readily appreciated if the liquid is in equilibrium with a phase such as olivine which is capable of incorporating both Fe²⁺ and Ni²⁺ into its crystal structure. Where this happens Ni²⁺ will partition more strongly into the olivine than Fe²⁺. This difference in the behavior of Ni and Fe is consistent with crystal-field theory. Ni²⁺ has 29.2 kcal/mole of crystal-field stabilization energy (CFSE) in octahedral sites but Fe²⁺ has only 11.9 kcal/mole. Two-thirds of the cation sites in olivine are octahedral, whereas in silicate melts tetrahedral sites are thought to predominate (Whittaker 1967), with sites of various other coordination numbers making up the balance. From size and crystal-field considerations Ni²⁺ and Fe²⁺ can be expected to occur predominantly in octahedral sites in the melt and to a lesser extent in other sites (from size consideration they are unlikely to enter tetrahedral sites in significant numbers). Ni²⁺, which receives the higher CFSE in octahedral sites, will be largely confined to those sites in the melt, whereas Fe²⁺ will have more tendency to "spill over" into other sites. The solubility of Ni in the melt is therefore less than that of Fe.

Both Ni^{2+} and Fe^{2+} will partition into olivine because it has a higher percentage of octahedral sites than the liquid, but Ni^{2+} , which receives more CFSE in sixfold coordination than Fe^{2+} , competes more successfully.

Roeder (1974) has shown that γ_{FeO} in a silicate liquid is increased by raising the Na_2O , K_2O , Al_2O_3 and, to a lesser extent, the SiO_2 content of the liquid. The data presented in this paper suggest that the same features control γ_{NiO} . Thus the high- Al_2O_3 , - Na_2O and - K_2O samples in Table 2, the dacite and the two andesites, have higher γ_{NiO} values than the basalts. Within the range of basaltic compositions studied, those with the highest $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O}$ contents also have the highest γ_{NiO} . This is not surprising, as Ni^{2+} and Fe^{2+} have similar chemical behavior and substitute into the same structural sites in minerals. They can therefore be expected to substitute into the same sites in melts, and factors affecting the structure of the melt will have a similar influence on both oxides.

It is apparent from the above discussion that increasing the acidity of the silicate liquid or raising its Si/O ratio (a measure of the acidity: Watson 1977) increases γ_{NiO} . This increase in γ_{NiO} with increasing acidity can be attributed to a decrease in the number of octahedral sites in the liquid or, alternatively, to a decrease in the number of silicate complexes containing octahedral sites.

The number of octahedral sites in the melt may not be the only factor affecting γ_{NiO} . If olivine and orthopyroxene coexist in a melt, partition coefficients for Ni^{2+} between olivine and the melt are about 3–4 times higher than those for orthopyroxene, whereas Fe^{2+} partition coefficients are similar in both minerals. These differences in the behavior of Ni^{2+} and Fe^{2+} are due to differences in the size and shape of the octahedral sites in olivine and orthopyroxene (Burns 1970). If the dominant complex in the melt changes from an olivine-like structure in ultramafic melts to a pyroxene-like structure in basalts (*cf.*, Irvine & Kushiro 1976), this change can be expected to contribute to the lower solubility of Ni^{2+} in basic melts compared with ultramafic melts but should have little effect on Fe^{2+} .

Our results show that γ_{NiO} is strongly temperature-dependent, whereas Roeder (1974) found that γ_{FeO} is not. This difference is, in part, due to the different choice of standard state for the two metals (solid for NiO and liquid for 'FeO'). Ideally, the comparison should be made using the same standard state in each case. As there are no thermodynamic data for liquid NiO we have recalculated Roeder's data for sample SY-MN using the solid stoichiometric 'FeO' as

the reference state. The enthalpy of fusion required for this calculation and the melting point for stoichiometric 'FeO' were taken from Robie *et al.* (1978). If liquid 'FeO' is used as the standard state, γ_{FeO} increases slightly with increasing temperature but decreases by 6% per 100°C increase in temperature if the solid is used as the standard state. Thus, although our use of different standard state exaggerates the difference between the temperature effect on γ_{FeO} and γ_{NiO} , the effect is real with γ_{NiO} being appreciably more temperature-dependent than γ_{FeO} .

It is unlikely to be a coincidence that Ni, the element with the higher CFSE in octahedral sites, is the most affected by temperature. We have already noted that the effect of increasing the acidity of the melt is to increase γ for both NiO and FeO, but the data in Table 2 suggest that the change is greater for Ni than Fe. Again the element with the higher CFSE in octahedral sites is the most affected. The unifying link between decreasing temperature and increasing acidity is that both result in an increase in the viscosity of the melt. In each case, this increase can be attributed to an increase in polymerization. It has been argued that the increase in γ_{NiO} with the acidity of the melt is due to a decrease in the number of octahedral sites. It is therefore tempting to suggest that the increase in degree of polymerization of the melt, which results from cooling, leads to a decrease in the number of octahedral sites. One possible explanation is to consider the melt as containing two dominant silicate complexes: pyroxene-like chains (or Ni-olivine-like complexes, depending on the composition of the melt: Irvine & Kushiro 1976) and feldspar-like frameworks. At high temperatures chains predominate but at lower temperatures framework structural complexes become increasingly important, resulting in a decrease in the number of octahedral sites.

If the linear relationship seen in Figures 1 and 2 is projected to higher temperatures, γ_{NiO} for each of the liquids becomes negative somewhere between 1550 and 1650°C (Fig. 3). This is theoretically impossible; we are therefore reluctant to project our results to temperatures above those covered by the experiments. We also caution against extrapolation of the results below 1200°C, as structural changes in the liquid may become increasingly important at lower temperatures.

APPLICATIONS

Olivine-liquid partition coefficient for nickel

The distribution of Ni between olivine and a

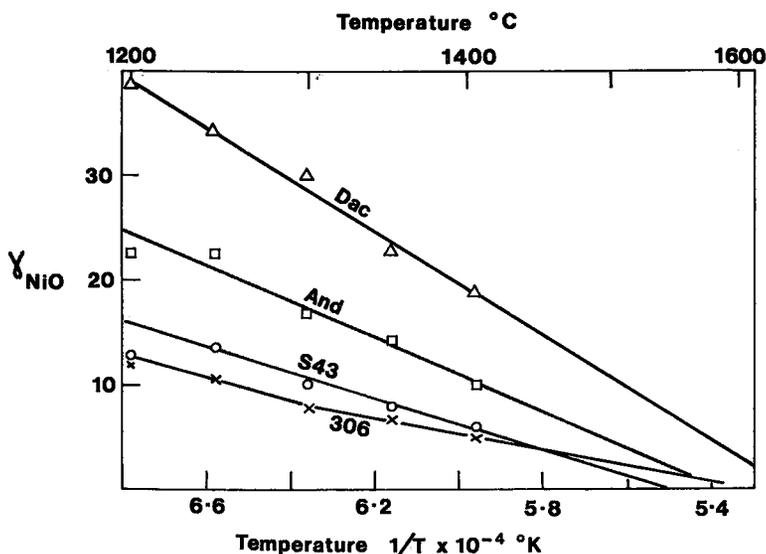


FIG. 3. The data from Fig. 1 projected to 1600°C, assuming a straight line relationship between γ_{NiO} and $1/T$ (K).

silicate liquid is usually expressed in terms of the Nernst partition coefficient:

$$D_w^{Ol} = \frac{\text{wt. \% NiO in olivine}}{\text{wt. \% NiO in liquid}} \quad (7)$$

$$\text{or } D_x^{Ol} = \frac{\text{mole fraction NiO in olivine}}{\text{mole fraction NiO in liquid}} \quad (8)$$

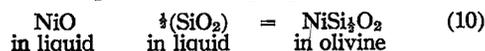
$$\text{where } D_w^{Ol} \approx 1.18 D_x^{Ol} \quad (9)$$

The partition is normally expressed as D_w^{Ol} in the geological literature but we have preferred to use D_x^{Ol} as it is more amenable to thermodynamic calculation.

There have been a number of experimental studies of the partitioning of Ni between olivine and silicate liquids. The results show that D_w^{Ol} increases with increasing acidity of the melt and with decreasing temperature, but the relative importance of temperature and composition is controversial. Häkli & Wright (1967), Irvine & Kushiro (1976) and Leeman & Lindstrom (1978) suggested that temperature exerts the dominant influence on D_w^{Ol} , with changes in composition playing a minor role, whereas Duke (1976) and Hart & Davis (1978) stress the role of composition. The problem is that it is impossible to change the temperature of a melt in equilibrium with olivine without changing its composition. Lowering the temperature, for example, results in the crystallization of additional olivine which changes the composition of the melt, making it more acidic.

Measurements of γ_{NiO} can be made above the

liquidus temperature, making it possible to independently assess the role of temperature and composition on this parameter. The relationship between λ_{NiO} and D_x^{Ol} has been demonstrated by Banno & Matsui (1973) and Duke & Naldrett (1977) using the following equation:



for which the equilibrium constant is:

$$K_{10} = \frac{a_{\text{NiSi}_3\text{O}_2}^{Ol}}{a_{\text{NiO}}^L \cdot (a_{\text{SiO}_2}^L)^{\frac{1}{2}}} = \frac{X_{\text{NiSi}_3\text{O}_2}^{Ol} \cdot \gamma_{\text{NiSi}_3\text{O}_2}^{Ol}}{X_{\text{NiO}}^L \cdot \gamma_{\text{NiO}}^L \cdot (a_{\text{SiO}_2}^L)^{\frac{1}{2}}} \quad (11)$$

Campbell & Roeder (1968) have shown that $\gamma_{\text{NiSi}_3\text{O}_2}^{Ol} = 1$ for low mole fractions of NiSi_3O_2 in the system MgSi_2O_2 - NiSi_3O_2 . The effect on $\gamma_{\text{NiSi}_3\text{O}_2}$ of iron substituting into olivine is not known, but assumed to be small, so that:

$$D_x^{Ol} = \frac{X_{\text{NiO}}^{Ol}}{X_{\text{NiO}}^L} = \frac{0.67 \text{ NiSi}_3\text{O}_2}{X_{\text{NiO}}^L} = 0.67 K_{10} (a_{\text{SiO}_2}^L)^{\frac{1}{2}} \gamma_{\text{NiO}}^L \quad (12)$$

0.67 being the mole fraction of NiO in NiSi_3O_2 .

From equation (12) it can be seen that D_x^{Ol} varies as a function of K_{10} , $(a_{\text{SiO}_2}^L)^{\frac{1}{2}}$ and γ_{NiO}^L ; K_{10} is approximately 1.0 and variations with temperature can be calculated for mineral assemblages that include a SiO_2 buffer, e.g., if olivine coexists with Ca-poor pyroxene. We have calculated the change in $(a_{\text{SiO}_2}^L)^{\frac{1}{2}}$ with temperature for the end-member assemblages forsterite-

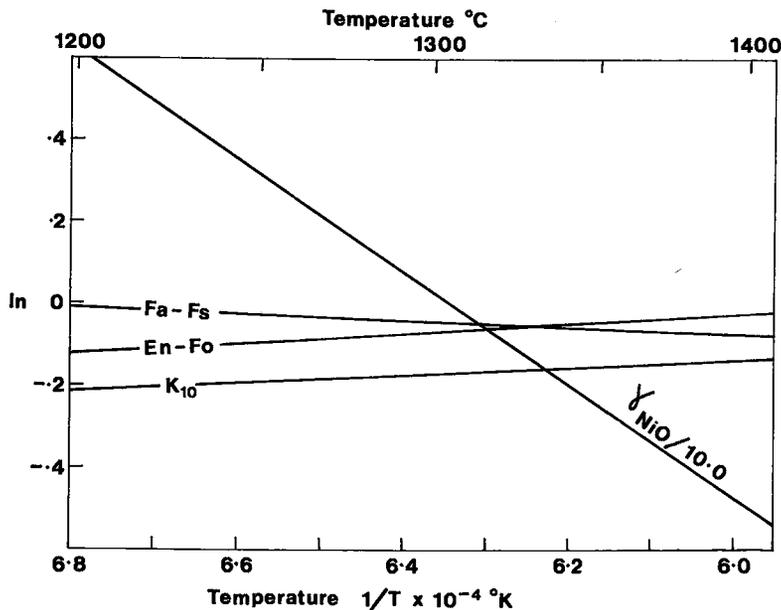


FIG. 4. Ln values for K_{10} , $\gamma_{NiO}^L/10$ and $(a_{SiO_2})^{1/2}$ for the buffer assemblages forsterite–enstatite (Fo–En) and fayalite–ferrosilite (Fa–Fs) plotted against $1/T$ (K).

enstatite (Fo–En) and fayalite–ferrosilite (Fa–Fs) (Fig. 4); $(a_{SiO_2})^{1/2}$ falls with decreasing temperature for the assemblage Fo–En but increases for Fa–Fs. The magnitude of the change is small in both cases, less than 5% per 100 K. Natural assemblages will lie between these two extremes (Campbell & Nolan 1974), making 5% per 100 K the maximum variation in $(a_{SiO_2})^{1/2}$ for natural coexisting olivine–Ca-poor pyroxene pairs.

The change in a_{SiO_2} in unbuffered assemblages is less readily assessed. Variations in tholeiitic melts are restricted (Carmichael *et al.* 1970), so that changes in this parameter are unlikely to have an important influence on $D_X^{O_i}$. However, in alkali basalts the influence of $(a_{SiO_2})^{1/2}$ on $D_X^{O_i}$ may be significant.

The relative influence of temperature on K_{10} , $(a_{SiO_2})^{1/2}$ and γ_{NiO}^L for melts in which the a_{SiO_2} is buffered by coexisting olivine and Ca-poor pyroxene can be assessed from Figure 4. It is apparent from this figure that γ_{NiO}^L is the principal factor controlling $D_X^{O_i}$ in basaltic liquids. Our experiments show that both temperature and composition of the liquid have an important influence on γ_{NiO}^L and hence on $D_X^{O_i}$; γ_{NiO}^L may increase by a factor of two if the temperature of the liquid is decreased by 130 K or if its composition is changed from a high-Mg basalt to an andesite, producing comparable changes in $D_X^{O_i}$.

TABLE 4. OLIVINE COMPOSITIONS

Temp. °C	1300	1300	1300	1203	1203
Sample	1868	P227	N144	P227	N138
SiO ₂	38.8	38.2	38.7	38.2	38.3
Al ₂ O ₃	0.8	0.6	0.6	0.4	0.1
FeO	6.6	7.2	7.2	7.5	10.0
MnO	0.1	0.2	0.1	0.2	0.1
MgO	37.5	36.4	36.0	37.0	36.4
CaO	0.2	0.4	0.3	0.4	0.2
NiO	16.9	16.5	17.4	15.2	14.5
Total	100.9	99.5	100.3	98.9	99.6
X _{NiO}	11.91	11.84	12.41	11.02	10.32
D _{X^{O_i}} ^{O_i}	6.0	6.5	7.0	14.5	11.0
D _{W^{O_i}} ^{O_i}	7.2	7.7	8.1	16.9	13.15

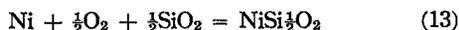
MOLE FRACTION

	1300	1300	1300	1203	1203
Mg _{1/2} SiO ₂	74.6	73.8	72.9	74.9	73.1
Fe _{1/2} SiO ₂	7.3	8.2	8.1	8.5	11.2
Ni _{1/2} SiO ₂	18.1	18.0	19.0	16.6	15.7
γ_{NiO}^L	.29	.30	.35	.33	.28
a_{SiO_2}	.66	.66	.72	.78	.71
γ_{NiO}^L	8.1	8.7	9.0	15.9	13.1
γ_{MgO}^L	.73	.74	.67	.91	.89

Synthetic olivines

Three of the 1300°C runs and two runs at 1203°C had olivine as a run product. Probe

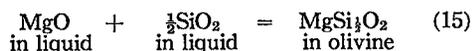
analyses of these grains are given in Table 4. The olivine composition can be used to calculate a_{SiO_2} of the liquid from the following equation:



This equation gives:

$$(a_{\text{SiO}_2})^{\frac{1}{2}} = \frac{K_{13} a_{\text{NiSi}\frac{1}{2}\text{O}_2}}{a_{\text{Ni}} f_{\text{O}_2}^{\frac{1}{2}}} \quad (14)$$

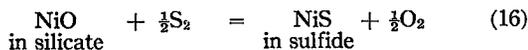
Values of a_{SiO_2} calculated from equation (14) range from 0.66 to 0.78 (Table 4). These values compare favorably with those obtained by Roeder (1974), which, when corrected for a computational error, lie between 0.5 and 0.9. It is also possible to calculate γ_{MgO} from equation (15) if $\gamma_{\text{MgSi}\frac{1}{2}\text{O}_2}$ is assumed to be one for high-Mg olivines (Campbell & Roeder 1968, Nafziger & Muan 1967):



The results, given in Table 4, vary between 0.67 and 0.91.

The partitioning of nickel between immiscible sulfide and silicate liquids

The distribution of Ni between immiscible sulfide and silicate liquids can be represented by the following exchange reactions:



for which the equilibrium constant is:

$$K_{16} = \frac{a_{\text{NiS}} f_{\text{O}_2}^{\frac{1}{2}}}{a_{\text{NiO}} f_{\text{S}_2}^{\frac{1}{2}}} \quad (17)$$

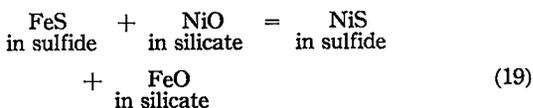
$$\text{giving: } D_{\text{Ni}}^{\text{sul}} = \frac{X_{\text{NiS}}}{X_{\text{NiO}}} = K_{16} \frac{\gamma_{\text{NiO}}}{\gamma_{\text{NiS}}} \frac{f_{\text{S}_2}^{\frac{1}{2}}}{f_{\text{O}_2}^{\frac{1}{2}}} \quad (18)$$

As our experiments show that γ_{NiO} increases with the acidity of the silicate liquid, $D_{\text{Ni}}^{\text{sul}}$ can be expected to be higher in an andesite than in a basalt. This prediction is in agreement with the work of Rajamani & Naldrett (1978) who showed that $D_{\text{Ni}}^{\text{sul}}$ at 1255°C increases from 274 in a basalt to 460 in an andesite. A similar argument can be used for Fe to show that $D_{\text{Fe}}^{\text{sul}}$ should also be higher in an andesite than in a basalt.

K_D for iron and nickel between immiscible sulfide and silicate liquids

The distribution of Fe and Ni between im-

miscible sulfide and silicate liquids can also be expressed in terms of the exchange reaction:



The relationship between the equilibrium constant for this reaction (K_{19}) and the distribution coefficient (K_D) is described by the equation:

$$K_{19} = \left(\frac{\gamma_{\text{NiS}}}{\gamma_{\text{FeS}}} \right)_{\text{sul liq}} \left(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{NiO}}} \right)_{\text{sil liq}} \times K_D \quad (20)$$

Citing the work of Scott *et al.* (1974) on the $\text{Fe}_{1-x}\text{S} - \text{Ni}_{1-x}\text{S}$ solid solution (MSS), Rajamani & Naldrett (1978) suggested that in liquids of the same composition as MSS, γ_{NiS} would have almost the same value as γ_{FeS} . For the range of MSS compositions for which this relationship holds, equation (20) simplifies to:

$$K_D = K_{19} \left(\frac{\gamma_{\text{NiO}}}{\gamma_{\text{FeO}}} \right)_{\text{sil liq}} \quad (21)$$

Theoretically, equation (21) can be used to calculate K_D for any silicate liquid in equilibrium with a sulfide liquid, provided γ_{NiO} and γ_{FeO} are known for the silicate liquid. This is a potentially valuable tool, as γ_{NiO} and γ_{FeO} are easier to determine experimentally than K_D . Unfortunately a practical difficulty arises with the calculation of K_{19} . Rajamani & Naldrett (1978) have shown that K_D for a basaltic liquid is 42 at 1255°C; γ_{NiO} should be close to 11 (Fig. 2) and γ_{FeO} , estimated from the work of Roeder (1974), is about 1.3. Substituting these values into equation (21) gives 5 as the approximate value for K_{19} . If K_{19} is calculated following the standard-state conventions and free-energy equations given in Table 1, a value of 16.9 is obtained. We prefer to be guided by experimental values. K_{19} is independent of composition; if K_D is determined experimentally for one silicate liquid of known a_{NiO} and a_{FeO} , it can be calculated and used for any other silicate liquid at the same temperature.

The effect of composition on K_D

It is apparent from equation (21) that K_D is proportional to the $\gamma_{\text{NiO}}/\gamma_{\text{FeO}}$ ratio in the silicate melt, provided the relationship $\gamma_{\text{NiS}} = \gamma_{\text{FeS}}$ holds in the sulfide liquid. However, because of the geochemical similarity between Fe^{2+} and Ni^{2+} , any change in melt composition which affects γ_{NiO} is likely to have a similar influence on γ_{FeO} . Thus, changes in the $\gamma_{\text{NiO}}/\gamma_{\text{FeO}}$ ratio in silicate liquids produced by compositional differences can be expected to be less than the change in

TABLE 5. K_{19} VALUES CALCULATED FROM THE FREE ENERGIES GIVEN IN TABLE 1

Temp. °C	1200	1300	1400	1500	1600
K_{19}	16.1	17.6	19.0	20.4	21.8

γ_{NiO} . Our experiments indicate that the range of γ_{NiO} values for basaltic liquids is small. K_D may therefore be regarded as insensitive to small compositional changes within the field of compositions of normal basaltic liquids.

An indication of the likely variation in the $\gamma_{\text{NiO}}/\gamma_{\text{FeO}}$ ratio between a basaltic and an andesitic liquid can be obtained from the work of Rajamani & Naldrett (1978). They found that K_D at 1255°C for a basaltic liquid is 42 and for an andesite is 59, an increase of 40%. According to equation (21), this increase is due to $\gamma_{\text{NiO}}/\gamma_{\text{FeO}}$ in the andesite being higher than in the basalt. It is interesting to note that $D_{\text{Ni}}^{\text{ml}}$, which is directly proportional to γ_{NiO} , is 70% higher in the andesite than in the basalt. $D_{\text{Fe}}^{\text{sul}}$ will also be higher in the andesite but, because $\gamma_{\text{NiO}}/\gamma_{\text{FeO}}$ is higher in the andesite than in the basalt, the percentage increase will be less.

The effect of temperature on K_D

The influence of temperature on K_D can be evaluated from equation (21), but again the difficulty in obtaining the correct value for K_{19} makes precise calculations impossible. The increase in K_{19} with temperature, as calculated from the data in Table 1, is about 10% per 100°C (Table 5). As demonstrated earlier, K_{19} can be calculated directly from the experimental determinations of K_D (Rajamani & Naldrett 1978) and from the results presented in this paper for the effect of temperature of γ_{NiO} ; γ_{FeO} is assumed to be independent of temperature (Fig. 5; Roeder 1974). This approach gives 20±20% as the increase in K_{19} per 100°C temperature increase. As γ_{NiO} falls by about 35% per

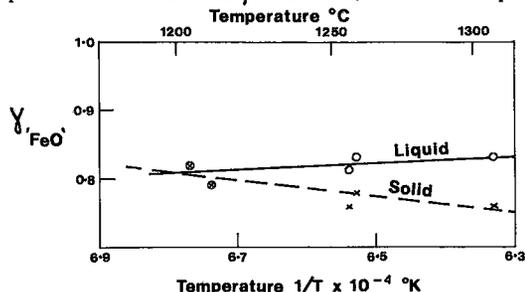


FIG. 5. The effect on γ_{FeO} of using liquid and solid standard states for stoichiometric 'FeO'. The data pertain to Roeder's (1974) sample SY-MN.

100°C rise in temperature (Figs. 1, 2), it seems likely that K_D decreases with increasing temperature by about 15±20% per 100°C.

CONCLUSIONS

It is apparent from this study that temperature and not composition is the dominant factor controlling γ_{NiO} in basaltic liquids. Distribution coefficients for Ni between basaltic liquids and silicate phases and between basaltic and sulfide liquids are controlled dominantly by γ_{NiO} . Temperature will therefore be the most important factor affecting these parameters in basaltic liquids, with small compositional changes having less influence. This does not mean that major compositional changes can be ignored. The value of γ_{NiO} at 1300°C is 5.0 in a fayalitic melt (Nagamori & Mackey 1978), 9 in a basaltic liquid and 30 in melts of rhyolite-dacite composition. Further systematic work is required to assess the role of composition on γ_{NiO} .

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